

The Oxygen Isotopic Exchange Reaction on Vanadium Oxide Catalysts

C. Doornkamp,* M. Clement,* X. Gao,† G. Deo,‡ I. E. Wachs,† and V. Poncec*,¹

*Leiden Institute of Chemistry, Leiden University, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, The Netherlands; †Zettlemoyer Center for Surface Studies, Departments of Chemical Engineering and Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015; and ‡Department of Chemical Engineering, Indian Institute of Technology, Kanpur, 208016, India

Received December 14, 1998; revised March 16, 1999; accepted March 18, 1999

The reactivity of lattice oxygen of vanadium oxide catalysts was studied with the oxygen isotopic exchange reaction. The reactivity of pure V_2O_5 is compared with the reactivity of $Li_{0.33}V_2O_5$, V_2O_5/TiO_2 , V_2O_5/Al_2O_3 , V_2O_5/SiO_2 , δ -VOPO₄, and $(VO)_2P_2O_7$. According to their behaviour in the oxygen exchange reaction, two types of vanadium oxide catalysts could be distinguished. The first type of catalysts only showed exchange activity in the R^2 exchange mechanism and the second type showed activity in both the R^1 and R^2 exchange mechanisms (mechanisms in which, respectively, one or two oxygen atoms of the gas phase molecule are exchanged with oxygen atoms of the metal oxide). The catalysts which belong to the first group are bulk V_2O_5 and δ -VOPO₄ and the catalysts which belong to the second group are $Li_{0.33}V_2O_5$, V_2O_5/TiO_2 , V_2O_5/Al_2O_3 , V_2O_5/SiO_2 , and $(VO)_2P_2O_7$. If only the R^2 mechanism is observed then diffusion of lattice oxygen is probably faster than when both the R^1 and R^2 mechanisms are observed. The activity of the supported vanadium oxide catalysts in the oxygen exchange reaction is dependent on the support. The reactivity order is $V_2O_5/TiO_2 > V_2O_5/Al_2O_3 \sim V_2O_5/SiO_2$.

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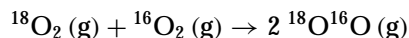
Key Words: oxygen isotopic exchange; supported vanadium oxide catalysts; VPO catalysts.

INTRODUCTION

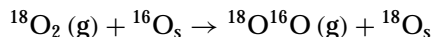
Vanadium oxide catalysts are frequently used in selective oxidation reactions. The most commonly posed question regarding these catalysts is “which factors make vanadium oxide catalysts so selective in some reactions compared to other metal oxides; is it only because of the high metal–oxygen bond strength or has the specific structure of the oxide also a large influence on its reactivity?” Compared to the other period IV metal oxides, V_2O_5 is the only oxide with a layer structure. V_2O_5 not only possesses two kinds of V–O–V bonds, but also a double bond, V=O. Several authors have tried to relate the activity and/or selectivity to either the V–O–V bond or the V=O bond of the oxide (1–5). However, despite extended structural, spectroscopic, and theoretical studies the role of both bond types is still debated.

Even in the oxygen isotopic exchange reaction, V_2O_5 behaves completely different compared to other period IV metal oxides (6). On metal oxides oxygen can be exchanged according to three different mechanisms (6–8):

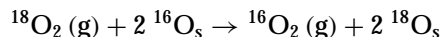
—the oxygen molecule exchanges one of its atoms with an atom of another oxygen molecule from the gas phase, without the participation of the oxide’s oxygen (R^0 mechanism).



—the oxygen molecule exchanges one of its atoms with the surface oxygen of the metal oxide (R^1 mechanism).



—the oxygen molecule exchanges both its atoms with the surface oxygen of the metal oxide (R^2 mechanism).



On V_2O_5 oxygen is only exchanged via the R^2 mechanism. All other oxides showed, depending on the temperature, apart from R^2 activity also exchange activity in the R^1 and/or R^0 mechanisms (6–8).

This deviating behaviour of V_2O_5 can be addressed to a difference in participation of lattice oxygen. In the case of V_2O_5 , all oxygen layers of the oxide take part in the exchange reaction, while in the case of the other oxides, only one to two layers of oxygen take part in the reaction. All these layers can participate, because diffusion of oxygen in V_2O_5 is much faster compared to that in other oxides. This was already mentioned by Jíru *et al.* and Boreskov *et al.* (9, 10). Thus, the preference of V_2O_5 for the R^2 mechanism can be possibly explained by the high mobility of oxygen in the lattice.

One can hope that a study of various vanadium oxide compounds might produce additional valuable information on the behaviour of V_2O_5 . For example, an element such as potassium or lithium can be added and in this way a vanadium oxide bronze is obtained. A vanadium oxide bronze is a nonstoichiometric compound in which vanadium has two

¹ To whom correspondence should be addressed.

different oxidation states, V^{4+} and V^{5+} . The amount of V^{4+} is equal to the amount of alkali metal. The layers of V_2O_5 in bronzes are more separated, since the alkali metal is situated between the V_2O_5 layers. Vanadium oxide bronzes have already been tested in the oxidation of CO and H_2 by van den Berg (11). Van den Berg observed a higher activity of the bronzes in both reactions compared to normal V_2O_5 and assigned this to the availability of V^{4+} in the bronze.

Supported vanadium oxide catalysts show a completely different behaviour in oxidation reactions than bulk V_2O_5 (12–14). Supported vanadium oxide catalysts are generally more selective and active for the partial oxidation of hydrocarbons than bulk V_2O_5 . The supports which are currently used are TiO_2 , Al_2O_3 , SiO_2 , and ZrO_2 .

Studies of supported vanadium oxide catalysts have revealed that at certain loadings vanadium oxide is present as a two-dimensional overlayer on the oxide support. This two-dimensional overlayer can be a monolayer coverage, but above the monolayer coverage V_2O_5 crystallites are also present. More fundamental information about the VO_x monolayers has been obtained by using various characterisation techniques, such as temperature programmed reduction (15, 16), Raman spectroscopy (17–19), Fourier transform infrared spectroscopy (FT-IR) (20, 21), electron paramagnetic resonance (EPR) (22), X-ray photoelectron spectroscopy (XPS) (23) and solid state NMR (24). Depending on the environmental conditions and on the loading of vanadium oxide, monomeric and/or polymeric vanadium oxide species are present on the surface. On the dehydrated silica supported vanadia catalyst only isolated VO_4 species are detected. These isolated species contain one terminal $V=O$ bond and three bridging $V-O-Si$ bonds. On the other supports, monomeric and polymeric structures are observed under dehydrating conditions. The isolated VO_4 units possess one $V=O$ bond and three $V-O$ -support bonds. The polymerised VO_4 units possess one terminal $V=O$ bond, one bridging $V-O$ -support bond and two bridging $V-O-V$ bonds. There may also be some octahedral coordinated species present at monolayer coverage.

It is believed that selective oxidation reactions on supported vanadium oxide catalysts proceed via a Mars and van Krevelen mechanism. The higher activity and selectivity of supported vanadium oxide catalyst in the partial oxidation of hydrocarbons with respect to bulk vanadium oxide is addressed to the higher reducibility of the supported vanadium oxide catalysts. However, there is still a debate about which $V-O$ bond ($V=O$ or $V-O-S$) is actually responsible for the redox properties of the supported catalysts.

Other very selective vanadium containing compounds are vanadium phosphorus oxides (VPO). VPO catalysts are used in the selective oxidation of *n*-butane to maleic anhydride. The active phase is generally considered to be $(VO)_2P_2O_7$, which consists of edge-sharing VO-octahedra connected by PO_4 tetrahedra.

The method by which the catalyst is prepared has a large influence on the activity and selectivity in the *n*-butane oxidation reaction. The VPO catalyst can be prepared from various precursors, such as $(VO)_2H_4P_2O_9$ (25) or $VOPO_4 \cdot 2H_2O$ (26) and $VO(H_2PO_4)_2$ (27). However, the most commonly used precursor is $VO(HPO_4) \cdot 0.5H_2O$. This precursor can be prepared in an aqueous solution or in an organic solution. The choice of solvent has a large influence on the morphology of the catalyst (28–30). The precursor is most often transformed into the active catalyst under a flow consisting of a mixture of oxygen and *n*-butane. On characterising the active VPO catalyst by XRD various phases have been detected, such as α - $(VO)_2P_2O_7$, β - $(VO)_2P_2O_7$, γ - $(VO)_2P_2O_7$, β - $VOPO_4$, γ - $VOPO_4$, δ - $VOPO_4$. Most authors think that one of the $(VO)_2P_2O_7$ phases is responsible for the activity of the reaction, but others think that a mixture of the $(VO)_2P_2O_7$ and $VOPO_4$ phases (31–36) is the most active and selective material.

One of the main features of the VPO catalyst is that, although the bulk composition of the active phase has a V : P ratio of 1 : 1, the surface is considerably enriched with phosphorus. Characterisation of the VPO catalyst also revealed that not only V^{4+} sites, but also V^{5+} sites are present in the active catalyst. Therefore, a mixture of phases might be necessary for the reaction to take place. The optimal V^{4+}/V^{5+} balance and the respective role of both species are still a matter of discussion (37).

Many authors have tried to elucidate the mechanism of the oxidation of *n*-butane on the VPO catalyst (38–46). It is generally accepted that this reaction, similarly to reactions on pure V_2O_5 , takes place via the Mars and van Krevelen mechanism, since oxygen from the VPO lattice is incorporated in the maleic anhydride formed. However, the nature of the active site and the individual steps of the reaction mechanism are still unknown.

In this article the oxygen exchange reaction was studied on the vanadium oxide bronze, on the supported vanadium oxides, and on the vanadium-phosphorus oxides (VPO), in order to compare the reactivity of lattice oxygen in these vanadium oxide catalysts.

EXPERIMENTAL

Sample Preparation

The $Li_{0.33}V_2O_5$ bronze was prepared by Mul (47). V_2O_5 was first prepared by decomposition of ammonium metavanadate in air at 623 K for 15 h. The bronze was synthesised by mixing V_2O_5 and Li_2CO_3 and treatment at 773 K in a nitrogen atmosphere for 15 h. The surface area of the bronze was very low, approximately $1 \text{ m}^2/\text{g}$.

The supported vanadium oxide catalysts are prepared by the incipient wetness impregnation method (48). The supported vanadium oxide catalysts are all approximately

TABLE 1

The Isotopic Exchange Reaction on Vanadium Oxide Catalysts at 823 K

Oxide	R^1 mechanism (molecules/m ² s)	R^2 mechanism (molecules/m ² s)
V ₂ O ₅		6.1 10 ¹⁴
Li _{0.33} V ₂ O ₅	5.8 10 ¹³	8.7 10 ¹⁴

monolayer coverage catalysts and crystalline V₂O₅ particles are absent. This was experimentally determined with Raman spectroscopy. The three supported vanadium oxides, which were tested in the isotopic exchange reaction, are 5% V₂O₅/TiO₂, 17.5% V₂O₅/Al₂O₃, and 9% V₂O₅/SiO₂.

The surface area of the supported vanadium oxides were determined by adsorption of nitrogen by using a quantasorb adsorption apparatus.

The oxygen isotopic exchange reaction was performed at 723 K. The exchange reaction could not be performed at higher temperatures, due to the expected instability of the V₂O₅ monolayer at higher temperatures. The possible contribution of the support to the activity in the isotopic exchange reaction was tested by performing the exchange reaction on pure TiO₂ and Al₂O₃ at 723 K.

The VPO catalyst can be prepared by activating the precursor VO(HPO₄) · 0.5H₂O. This precursor was prepared by the method of Busca *et al.* (28). Fifteen grams of V₂O₅ was reduced in a mixture of 90 ml isobutyl alcohol and 60 ml benzyl alcohol for 3 h under reflux. Subsequently, 18.9 g of 15% orthophosphoric acid was added. This mixture was stirred under reflux overnight. The resulting blue solution was filtered and washed with isobutanol and ethanol. The substrate was dried in air at 423 K. The green powder was characterised with XRD and found to be VO(HPO₄) · 0.5H₂O.

The VO(HPO₄) · 0.5H₂O precursor was activated under various conditions. Two samples were activated under a nitrogen flow at 713 K for 6 and 15 h respectively. Two other samples were activated under an oxygen flow at 773 and 873 K for, respectively, 5 and 15 h. The resulting phases of

the obtained VPO catalysts were characterised by XRD. The surface areas of the VPO catalysts were determined by adsorption of nitrogen.

The Oxygen Isotopic Exchange Reaction

The oxygen isotopic exchange reactions were carried out in a high vacuum system made from glass. A mixture of ¹⁸O₂ (Isotec Inc., 99.1% ¹⁸O) and ¹⁶O₂ (Messer Griesheim) was added to the reactor and the concentration of all three isotopes in the gas phase was followed with time by a mass spectrometer (VG instruments 8–80 mm) via a continuous leak. The pressure decrease was negligible during the experiment. The reactor was made of quartz and had a volume of 912 ml. The total oxygen pressure was 0.9 mbar.

Before the exchange reaction was performed, the vanadium oxide catalyst was treated by a standard pretreatment, i.e., 3 h evacuation at the temperature of the reaction, followed by 3 h of equilibration with 1 mbar ¹⁶O₂ at the temperature of the reaction. The rate constants of the exchange mechanisms were determined by fitting the kinetic equations to the experimental data (6).

RESULTS

Vanadium Oxide Bronze

The isotopic exchange reaction on Li_{0.33}V₂O₅ is compared with the exchange reaction on pure V₂O₅ and the results are shown in Table 1. No R^0 exchange activity is observed on Li_{0.33}V₂O₅. However, in contrast to V₂O₅, the vanadium oxide bronze shows some activity in the R^1 exchange mechanism. The total exchange rate, $R^1 + R^2$, is also slightly larger on Li_{0.33}V₂O₅ than on V₂O₅.

Supported Vanadium Oxide Catalysts

If the oxygen isotopic exchange reaction is performed on supported vanadium oxide, no R^0 exchange activity is observed. Oxygen is exchanged via the R^1 and R^2 mechanisms, as is the case of the vanadium oxide bronze. The exchange rates are presented in Table 2. The exchange rates are

TABLE 2

Isotopic Exchange Reaction on Supported Vanadium Oxide Catalysts at 723 K

Oxide	TOF (s ⁻¹) R^1 mechanism	TOF (s ⁻¹) R^2 mechanism	R^1 mechanism (molecules/m ² s)	R^2 mechanism (molecules/m ² s)
5% V ₂ O ₅ /TiO ₂	2 10 ⁻⁶	3 10 ⁻⁶	1.8 10 ¹³	2.2 10 ¹³
17.5% V ₂ O ₅ /Al ₂ O ₃	4 10 ⁻⁹	1 10 ⁻⁸	1.0 10 ¹¹	2.5 10 ¹¹
9% V ₂ O ₅ /SiO ₂	3 10 ⁻⁸	6 10 ⁻⁸	9.2 10 ¹⁰	2.1 10 ¹¹
V ₂ O ₅	—	—	—	8.1 10 ¹²
TiO ₂	—	—	—	—
Al ₂ O ₃	—	—	1.5 10 ¹²	2.5 10 ¹²
SiO ₂	—	—	—	—

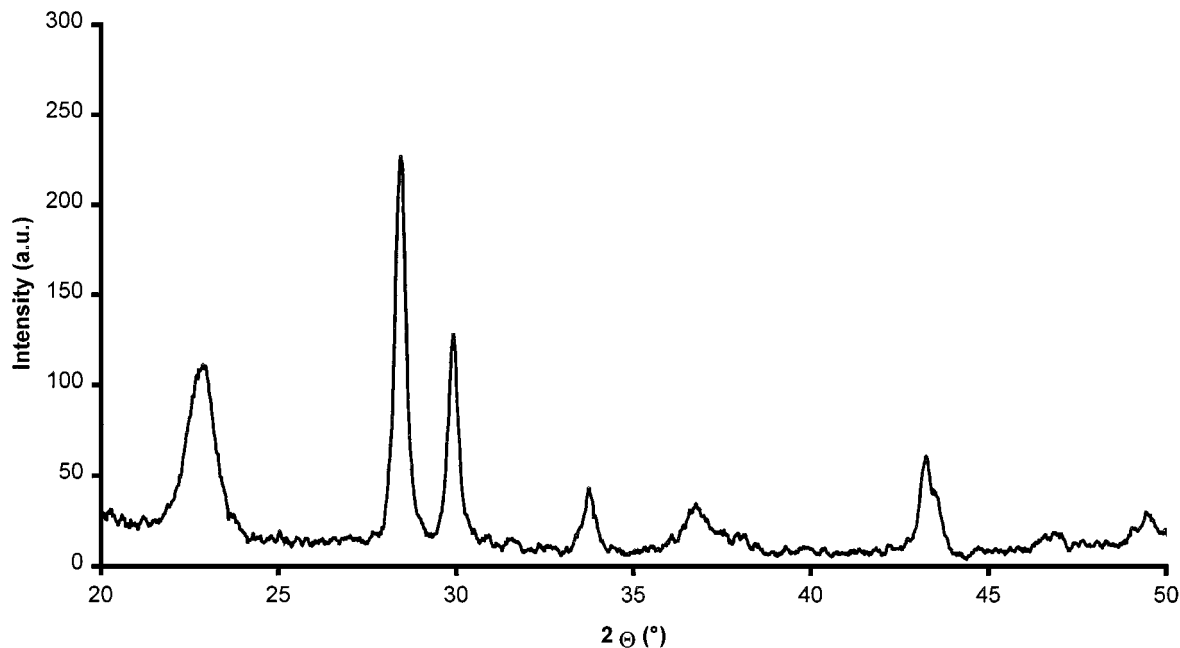


FIG. 1. XRD pattern of $(\text{VO})_2\text{P}_2\text{O}_7$.

presented as TOF (s^{-1}), which is the moles of oxygen exchanged per mole V^{5+} , and as rates in units of molecules/ $\text{m}^2 \text{s}$.

During the exchange reaction on $\text{V}_2\text{O}_5/\text{SiO}_2$, an increase of mass 18 was observed, while the concentration of $^{18}\text{O}_2$ decreased during the exchange experiment. If mass 18 is only a fragmentation peak of $^{18}\text{O}_2$ a decrease of mass 18 would be expected. The increase of mass 18 can be explained by dehydration of the $\text{V}_2\text{O}_5/\text{SiO}_2$ sample during the exchange reaction. This dehydration of the sample did not seem to have any influence on the exchange rates, since the exchange rates stayed constant during the whole experiment.

The supports of the vanadium oxide catalyst do not probably contribute to the exchange activity, since on TiO_2 and SiO_2 no exchange activity is observed at 723 K. The question is if Al_2O_3 contributed to the exchange activity of $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$. Vuurman *et al.* (19) determined with Raman spectroscopy that with loadings above 20%, monolayer coverage has been exceeded and crystalline V_2O_5 particles were detected on $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$. Thus on the $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ sample the surface area of aluminium oxide is maximally covered with vanadium oxide species. Therefore if Al_2O_3 contributed to the exchange rate this contribution is probably very small.

VPO Catalyst

The precursor for the VPO catalyst was characterised with XRD and a comparison with literature showed that the precursor was $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$. The precursor was calcined under nitrogen and oxygen, respectively. The cal-

ination time and temperature (in case of activation under oxygen) did not have any influence on the bulk structure of the samples. The XRD patterns were similar. The XRD pattern after calcination under nitrogen and oxygen are shown in Figs. 1 and 2.

The XRD recorded after calcination under nitrogen was compared with the XRD pattern presented in the literature. It appeared that the pattern in Fig. 1 is in correspondence with that of the $(\text{VO})_2\text{P}_2\text{O}_7$ phase. The pattern in Fig. 2 was compared with the XRD pattern of Ben Abdelouhab *et al.* (32) and it appeared that this pattern corresponds to the $\delta\text{-VOPO}_4$ phase.

After calcination of the precursor in oxygen and nitrogen, respectively, the isotopic exchange reaction was performed at 823 K on the thus prepared VPO catalysts. The results are shown in Table 3. In the first column of Table 3 the activation conditions of the precursor are presented. The $(\text{VO})_2\text{P}_2\text{O}_7$ compound shows exchange activity in the R^1 and R^2 exchange mechanisms. On the other hand the

TABLE 3
Oxygen Exchange Reaction on VPO Catalysts at 823 K

Calcination temp.	precursor	VPO phase	Surface area (m^2/g)	R^1 mechanism (molecules/ $\text{m}^2 \text{s}$)	R^2 mechanism (molecules/ $\text{m}^2 \text{s}$)
713 K	(N_2 15 h)	$(\text{VO})_2\text{P}_2\text{O}_7$	18.9	$8.8 \cdot 10^{12}$	$8.5 \cdot 10^{13}$
713 K	(N_2 5 h)	$(\text{VO})_2\text{P}_2\text{O}_7$	20.9	$2.2 \cdot 10^{12}$	$8.7 \cdot 10^{13}$
713 K	(O_2 6 h)	$\delta\text{-VOPO}_4$	5.5	—	$2.7 \cdot 10^{13}$
873 K	(O_2 15 h)	$\delta\text{-VOPO}_4$	14.1	—	$1.2 \cdot 10^{13}$

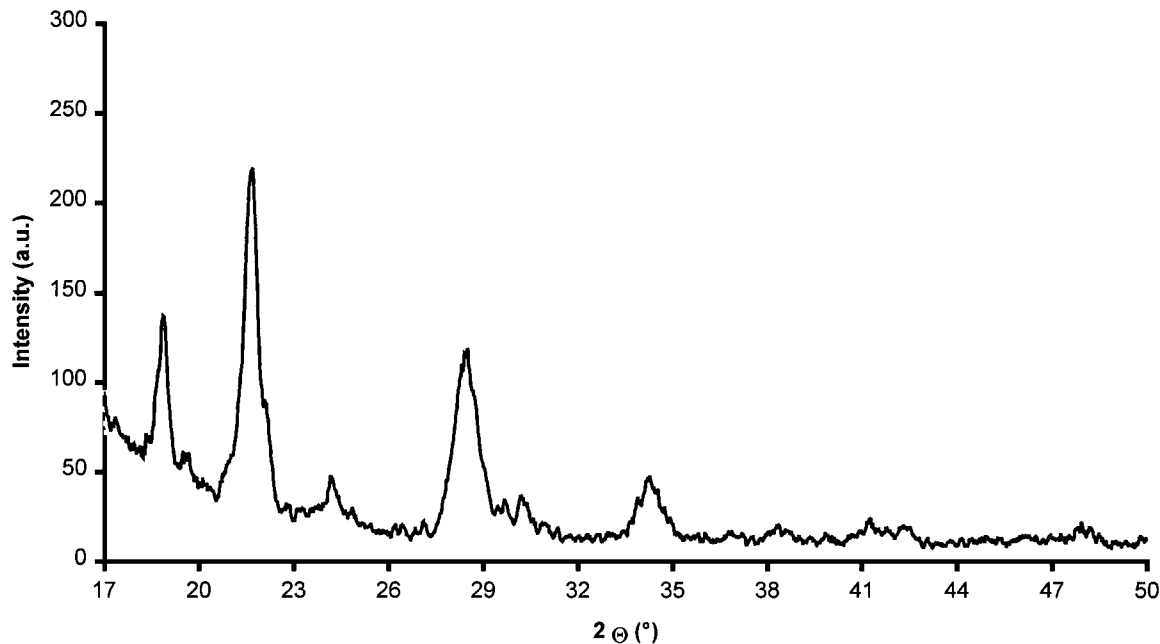


FIG. 2. XRD pattern of δ -VOPO₄.

δ -VOPO₄ compound only shows exchange activity in the R^2 exchange mechanism. Table 3 also reveals that the overall oxygen exchange rate is larger for the (VO)₂P₂O₇ phase than for the δ -VOPO₄ phase.

Since the oxygen exchange reaction is performed under oxidising conditions and the sample was pretreated in oxygen, a possible change in the (VO)₂P₂O₇ phase was checked with XRD after the exchange reaction was performed. Although the XRD pattern still showed that the sample only consisted of the (VO)₂P₂O₇ phase, it is still possible that the surface of the catalyst was oxidised.

DISCUSSION

The R^1 and R^2 Exchange Mechanisms on Vanadium Oxide Catalysts

The isotopic oxygen exchange reaction was studied on various vanadium oxide catalysts. According to their behaviour in the oxygen exchange reaction, two types of vanadium oxide catalysts can be distinguished. The first type of catalysts only show exchange activity in the R^2 exchange mechanism and the second type exhibit activity in the R^1 and R^2 exchange mechanisms. The catalysts which belong to the first group are bulk V₂O₅ and δ -VOPO₄ the catalysts which belong to the second group are Li_{0.33}V₂O₅, V₂O₅/TiO₂, V₂O₅/Al₂O₃, V₂O₅/SiO₂, and (VO)₂P₂O₇.

The results of the oxygen exchange reaction on the period IV metal oxides showed that the R^1 and R^2 mechanisms are mutually related (6). All period IV metal oxides exchange oxygen via the R^1 and R^2 exchange mechanisms and their

activity differs not more than by one to two orders of magnitude. The question which arises is in which way V₂O₅ and δ -VOPO₄ differ from the other vanadium oxides that oxygen is only exchanged via the R^2 mechanism.

Two vacancies are required for the R^2 exchange mechanism to take place. There are two ways in which these vacancies become available. (i) The double vacancies are already present at the surface of V₂O₅. The concentration of oxygen vacancies in the surface layer of oxides is mostly larger than the concentration in the bulk. Especially in the case of V₂O₅, since the exchange reaction is performed at temperatures which are close to the melting point of V₂O₅ (963 K) and the double vacancies will be more stable at the surface. Therefore it is possible that double vacancies are present on the surface of V₂O₅. (ii) The second way the R^2 mechanism can proceed is that a single vacancy is required for adsorption of the oxygen molecule, but the second vacancy diffuses very quickly from the bulk of the oxide to the surface and two vacancies are available for the R^2 exchange mechanism. In this case the R^2 mechanism only takes place if the diffusion of vacancies is very fast. If diffusion of the second vacancy is not fast enough, the probability that the oxygen molecule exchanges its atoms via the R^1 mechanism increases.

The difference between the first and second group of vanadium oxide catalysts is thus probably due to the different diffusion rates of lattice oxygen. Addition of an alkali metal seems to reduce the mobility of oxygen in the lattice. The same conclusion was drawn by Mul (47). Mul performed carbothermic reduction experiments with V₂O₅ and a vanadium oxide bronze and observed that the bronze is reduced at higher temperatures than bulk V₂O₅. Mul also

observed a lower activity of the bronze in the soot oxidation. He concluded that the higher reduction temperature of $\text{Li}_{0.33}\text{V}_2\text{O}_5$ and its lower activity in the soot oxidation was caused by a reduced mobility of lattice oxygen.

The same conclusion can be drawn in the case of the supported vanadium oxide catalysts. Compared to bulk V_2O_5 , diffusion in supported V_2O_5 is probably much slower, since no bulk oxygen is available in supported V_2O_5 and the vanadium oxide species are bound to the support.

In conclusion, if diffusion of lattice oxygen in vanadium oxide catalysts is slow, oxygen is exchanged via both the R^1 and R^2 exchange mechanisms. If diffusion is very fast then only R^2 exchange activity is observed on vanadium oxide catalyst.

Activity of Supported Vanadium Oxide Catalysts

Table 2 shows that at 723 K the activity of the oxygen isotopic exchange reaction on V_2O_5 is comparable with the activity on $\text{V}_2\text{O}_5/\text{TiO}_2$. The exchange activity on $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and on $\text{V}_2\text{O}_5/\text{SiO}_2$ is on the other hand more than one order of magnitude smaller than on V_2O_5 . This in contrast to the partial oxidation reactions of hydrocarbons, which normally show a higher activity of the supported vanadium oxide catalysts with respect to bulk V_2O_5 . This higher activity of supported vanadium oxide catalyst is addressed to the higher reducibility of the vanadium oxide surface species.

One thing which should be taken into account when comparing the oxygen exchange reaction with partial oxidation reaction is the reduction state of the surface. The oxygen exchange reaction is performed under oxidising conditions and partial oxidation reactions take place under more reduced conditions. Under reducing conditions more vanadium oxide species are partly reduced which are able to activate gas phase oxygen. A similar behaviour is also observed on pure metal oxides in the oxygen exchange reaction. The activity of the oxygen isotopic exchange reaction is increased when the surface of the metal oxides is partially reduced (6).

There is a certain similarity between the oxygen exchange reaction and the partial oxidation reactions. As with partial oxidation reactions, the activity in the oxygen exchange reaction is also strongly influenced by the type of support. The reactivity order of the supported vanadium oxide catalyst in the oxygen exchange reaction is $\text{V}_2\text{O}_5/\text{TiO}_2 > \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 \sim \text{V}_2\text{O}_5/\text{SiO}_2$.

A similar reactivity order is found in the literature for several partial oxidation reactions. Deo *et al.* (48) determined the reactivity of several supported vanadium oxide catalysts (Al_2O_3 , Nb_2O_5 , SiO_2 , TiO_2 , ZrO_2) in the partial oxidation of methanol. The observed reactivity order was $\text{V}_2\text{O}_5/\text{ZrO}_2 > \text{V}_2\text{O}_5/\text{TiO}_2 > \text{V}_2\text{O}_5/\text{Nb}_2\text{O}_5 > \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 > \text{V}_2\text{O}_5/\text{SiO}_2$.

The turnover frequency of methanol varied by two to three orders of magnitude when the support was changed from ZrO_2 to SiO_2 . Deo *et al.* also determined the reduc-

bility of the supported V_2O_5 by a temperature programmed reduction. They found a relationship between the reducibility of the supported V_2O_5 catalyst and the activity of the catalyst in the partial oxidation of methanol to formaldehyde. The higher the activity in the methanol oxidation reaction, the lower the maximum reduction temperature. Deo *et al.* (48) suggest that the reduction reaction takes place preferentially at the V–O–support bond and that a higher reduction temperature is most probably due to a greater V–O–S bond strength. Thus, the relationship between the activity in the methanol oxidation reaction and the reducibility of the supported vanadium oxide catalyst suggests that the activity in the methanol reaction is also determined by the V–O–support bond strength.

The above mentioned reaction order for supported vanadium oxide catalysts was also found for the partial oxidation of butane to maleic anhydride (49). Also in the reduction of NO with NH_3 on 1% V_2O_5 supported catalysts an influence of the support on the reactivity was found (50), although the difference was only a factor 3 in the turnover frequency, which is much less compared to the oxidation of butane and methanol.

Mori *et al.* (51) tested the selective oxidation of benzene on supported vanadium oxide catalysts. They found a higher TOF for $\text{V}_2\text{O}_5/\text{TiO}_2$ ($\text{TOF} = 101 \text{ ks}^{-1}$) than for $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ ($\text{TOF} = 30 \text{ ks}^{-1}$). Mori *et al.* (52) also found higher TOFs for $\text{V}_2\text{O}_5/\text{TiO}_2$ than for $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ in the oxidation of buta-1,3-diene and but-1-ene. However, contrary to other authors they concluded that the activity was proportional to the amount of V=O species on the catalyst surface.

In conclusion, the reactivity order of the supported vanadium oxide catalysts in the oxygen exchange reaction is in general in agreement with the reactivity order of these catalysts in various oxidation reactions. Since the activity of oxygen exchange reaction is also a reflection of the average metal–oxygen bond strength, the results reveal indirectly the influence of the support on the reactivity of the surface lattice oxygen in the vanadia monolayers. The results of the oxygen exchange reaction are thus in accordance with the ideas of Deo *et al.* (48) that the V–O–support bond is primarily responsible for the reactivity of the supported vanadium oxides.

Selectivity of Supported Vanadium Oxide Catalysts

If the selectivity in the oxidation reaction on the supported vanadium oxides is compared with the activity, then for most reactions the supported vanadium oxide with the highest activity also shows the highest selectivity to the desired product. Mori *et al.* observed a higher selectivity to maleic anhydride in the oxidation of benzene, buta-1,3-diene, and but-1-ene on $\text{V}_2\text{O}_5/\text{TiO}_2$ than on $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$.

The selectivity order in the reaction of methanol to formaldehyde is $\text{V}_2\text{O}_5/\text{TiO}_2 > \text{V}_2\text{O}_5/\text{SiO}_2 > \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$. Although the reactivity of $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ is higher than that

of V_2O_5/SiO_2 , the selectivity to formaldehyde is lower, since V_2O_5/Al_2O_3 shows a high selectivity to dimethyl ether.

In contrast to these results, in the case of the oxidation of *n*-butane to maleic anhydride, the vanadium support with the highest activity shows the lowest selectivity to maleic anhydride. For this reaction the selectivity order is $V_2O_5/SiO_2 > V_2O_5/Al_2O_3 > V_2O_5/TiO_2$.

It seems that although the activity of supported vanadium oxide catalysts is determined by the strength of the V–O–S bond, the selectivity is much less influenced by the bond strength. This is in contrast to other selective oxidation reactions on pure metal oxides, in which a higher M–O bond strength leads to a lower activity, but usually to a higher selectivity.

On supported metal oxides there is no large reservoir of bulk oxygen which is able to abstract many hydrogen atoms. According to Sachtler *et al.* (53, 54) the selectivity in the Mars and van Krevelen oxidation reactions is determined by two factors: (1) by the intrinsic activity of individual oxygen species, (2) by their availability, i.e., the first one or two oxygen atoms must be reactive, but the other lattice oxygens must be nonreactive, since only then the oxidation stops at the desired level of a partially oxidised product. Abstraction of many hydrogen atoms from the hydrocarbon will lead to a breaking of C–C bonds and consequently to complete oxidation. Thus, the locally limited amount of reactive lattice oxygens might be the explanation for the high selectivity of supported metal oxides.

The δ -VOPO₄ and (VO)₂P₂O₇ Phases of the VPO Catalyst

Table 3 shows that the $(VO)_2P_2O_7$ phase of the VPO catalyst exchanges oxygen via the R^1 and R^2 exchange mechanisms and that the δ -VOPO₄ phase only exchanges oxygen via the R^2 mechanism. The absence of the R^1 exchange activity on δ -VOPO₄ probably suggests that the mobility of oxygen vacancies is larger in δ -VOPO₄ than in $(VO)_2P_2O_7$. However, the reactivity of both phases should be studied in more detail to see if this conclusion is definitive.

The oxidation state of vanadium in the δ -VOPO₄ phase is V^{5+} , while the oxidation state of vanadium in the $(VO)_2P_2O_7$ phase is V^{4+} . The difference in oxidation states might have an effect on the exchange mechanisms, but the relation of the oxidation state of a metal oxide to the oxygen exchange rate is still unknown and it is difficult to speculate any further on this topic. The results on the oxygen exchange reaction on metal oxides only show that if more vacancies are created on the surface of the metal oxide, the activity in the oxygen exchange reaction increases.

Most authors consider the $(VO)_2P_2O_7$ phase to be active in the oxidation reaction of *n*-butane to maleic anhydride. As already mentioned in the Introduction, it is generally accepted that the reaction takes place via the Mars and van Krevelen mechanism and some authors detected V^{5+}

in the active phase. Abon *et al.* (40) showed with labelling studies that only surface lattice oxygen is responsible for the formation of maleic anhydride, CO, CO₂, and H₂O in the oxidation of butane on the VPO catalyst.

On the other hand Volta *et al.* (35) claim that a biphasic catalyst consisting of $(VO)_2P_2O_7$ and VOPO₄ is the catalytic active phase. By using Raman spectroscopy, Volta *et al.* studied the decomposition of the $VO(HPO_4) \cdot 0.5H_2O$ precursor and its structure after activation of it in *n*-butane and air. They found that maleic anhydride is produced when the VOPO₄ and the $(VO)_2P_2O_7$ phases are simultaneously present. When increasing the temperature of activation from 643 up to 683 K the Raman spectra showed that the δ -VOPO₄ phase was changed into the α_{II} -VOPO₄ phase. The authors concluded that various processes were occurring in the course of the activation of the VPO catalyst and a model was proposed to explain it.

The observations of Volta *et al.* suggest that the VOPO₄ phase and the $(VO)_2P_2O_7$ phase behave as a redox couple. To test this possibility the $(VO)_2P_2O_7$ phase was treated in oxygen at 873 K for 15 h and the XRD pattern revealed that the δ -VOPO₄ phase was obtained. It is therefore possible that the surface of the active VPO catalyst consists of a mixture of both phases, creating in this way the optimal V^{4+}/V^{5+} balance and the optimal reactivity of lattice oxygen.

Table 3 shows that the total exchange rate is approximately one order of magnitude larger on $(VO)_2P_2O_7$ than on δ -VOPO₄. This means that the reactivity of lattice oxygen is larger for the $(VO)_2P_2O_7$ phase than for the δ -VOPO₄ phase.

Since the exchange activity of the δ -VOPO₄ phase is lower than the $(VO)_2P_2O_7$ phase, the average M–O bond in the δ -VOPO₄ phase is probably stronger than the average M–O bond in the $(VO)_2P_2O_7$ phase. A mixture of both phases might therefore lead to an optimum M–O bond strength for the oxidation of *n*-butane to maleic anhydride.

CONCLUSIONS

The oxygen isotopic exchange reaction was studied on various vanadium oxide catalysts. According to their behaviour in the oxygen exchange reaction, two types of vanadium oxide catalysts could be distinguished. The first type of catalysts only showed exchange activity in the R^2 exchange mechanism and the second type showed activity in both the R^1 and R^2 exchange mechanisms. The catalysts which belong to the first group are bulk V_2O_5 and δ -VOPO₄ and the catalysts which belong to the second group are $Li_{0.33}V_2O_5$, V_2O_5/TiO_2 , V_2O_5/Al_2O_3 , V_2O_5/SiO_2 , and $(VO)_2P_2O_7$.

The R^1 exchange activity is only observed on vanadium oxide catalysts when diffusion of lattice oxygen is slow enough for the R^1 exchange mechanism to be able to appear. If diffusion of vacancies is high, as is the case for V_2O_5 , then only R^2 exchange activity is observed.

The activity of the oxygen isotopic exchange reaction on supported vanadium oxide catalysts is dependent on the support. The reactivity order of the supported vanadium oxide catalyst is $V_2O_5/TiO_2 > V_2O_5/Al_2O_3 \sim V_2O_5/SiO_2$. Comparing this result with literature data showed that the reactivity order of the supported vanadium oxide catalysts in the oxygen exchange reaction is in general the same as the reactivity order of these catalysts in various oxidation reactions. The activity of the supported vanadium oxide catalysts in the oxygen exchange reaction is thus probably determined by the reactivity of the V-O-support bond.

The isotopic exchange reaction was studied on two types of VPO phases ($(VO)_2P_2O_7$ and δ -VOPO₄), which could both be prepared from the same precursor $(VO(HPO_4) \cdot 0.5H_2O)$. The δ -VOPO₄ only showed exchange activity in the R^2 exchange mechanism, while $(VO)_2P_2O_7$ showed exchange activity in the R^1 and R^2 exchange mechanisms. The total exchange activity on the $(VO)_2P_2O_7$ phase is also larger than on the δ -VOPO₄ phase, indicating a stronger average M-O bond strength for the δ -VOPO₄ phase. By oxidising the $(VO)_2P_2O_7$ phase at elevated temperatures the δ -VOPO₄ can be obtained. Extensive studies on VPO catalyst in literature and the results of the isotopic exchange reaction suggest that the $(VO)_2P_2O_7$ and δ -VOPO₄ phases are a redox couple and that a mixture of both phases is responsible for a high activity and selectivity of the VPO catalyst in the oxidation of *n*-butane to maleic anhydride.

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